# Insulating Biomaterials
# N01-NS-62350

## Ninth Quarterly Progress Report
## October-December, 1998

**Submitted to:**

## Neural Prosthesis Program
**National Institutes of Health**
**National Institute of Neurological**
**Disorders and Stroke**

**By the:**


## Biomedical Microelectronics Laboratory
**Biomedical Engineering Center, Massachusetts Institute of Technology**
**West Roxbury VA Medical Center**

**Contributors:**
**David J. Edell, PI**
**Karen K. Gleason, Chemical Engineering**
**Bruce C. Larson, Grad Student, Electrical Engineering**
**Hilton Lewis, Grad Student, Chemical Engineering**
**Sean Sexton, Electronics**
**Cynthia M. Vanaria, Assembly**

## Introduction

The Insulating Biomaterials contract work remains focussed on screening promising materials while developing a detailed understanding of a few promising silicone materials. Recent advances in design of a CMOS monitoring system will soon allow evaluation of the critical components of CMOS integrated circuits that have been encapsulated with test materials and implanted in animals. This monitoring system will transmit data by telemetry thereby eliminating all of the issues associated with long term implantation of skull mounted percutaneous connectors for this application.

This report summarizes some improvements in instrumentation, some attempts at making animal implant test devices using PPECVD silicone coatings, mechanical properties of silicones, silicone adhesion studies, silicon substrate studies and CMOS integrated circuit tester progress.

## Instrumentation

Now that the 384 channel electrometer system has been in operation for nearly one year, the performance of the system can be evaluated. Perhaps the simplest evaluation is an open circuit test where there is no device attached to the system while the measurements are taken. An example of open circuit data from an unused set of electrometers is shown in Figure 1. In this particular case, a 3 foot long extension cable typical of those used to connect to older devices was left in place with no device plugged into it. From this data it is clear that while there is some noise associated with the measurements, it should be possible to reliably monitor resistance levels up to $10^{15}\Omega$. This data could also be smoothed considerably with more data points which will allow more sensitive detection of trends in the future.

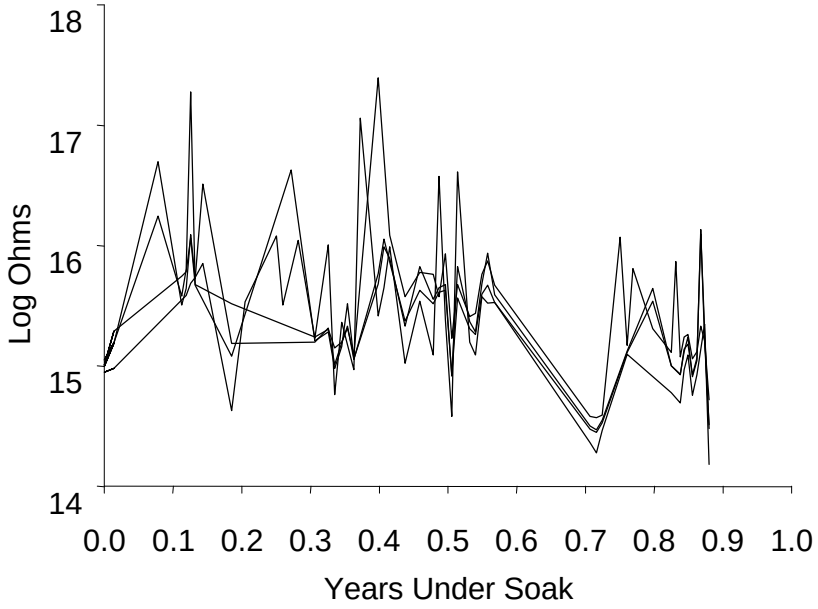



**Figure 1:** Open circuit data for one set of 4 electrometers in high temperature soak system. Data acquired with 3-foot connection cable in place that is used for connecting to older type jars.

In order to increase the frequency of measurements, a new computer was installed for the long term testing system. Previously, the 486-66 computer required over 2 hours to complete one data point. With 42 data points per sweep, the cycle time between measurements was about 4 days. The new computer completes the measurements in 2 days which is now set by the settling time requirements for the system after each voltage change during the sweep.

Long-term soak data from prior years were converted to the new data format and added to the data files being acquired with the new test system. This allows us to continue monitoring devices that have been under soak for many years. Figure 2 shows the results for two such devices. The much more frequent sampling beginning one year ago allows for better trend analyses. The recent changes in the system now measures the resistance of each device every 2 days which is only evident in the last few samples of each data set.

One of the 64 channel electrometer boxes was modified by decreasing the resistor to $10^{10}\Omega$ and post amplifier gain to 1 to allow measurement of lower resistance devices such as the silicone test devices.

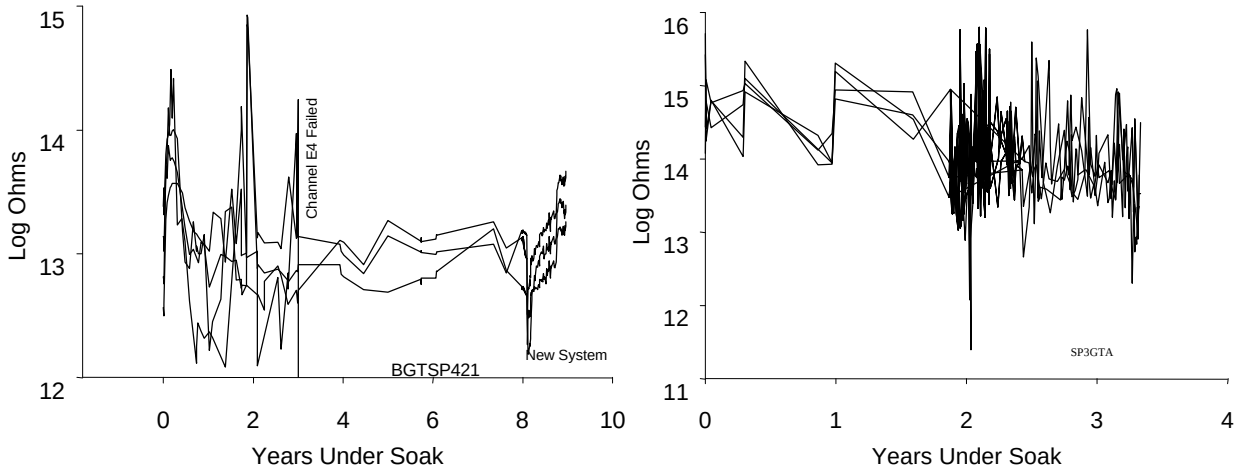



**Figure 2:** Example data sets from compiled results of long term soak testing with older single channel system based on the Keithley 617 electrometer, and the new 384 channel system based on discrete electrometer op-amps. The new system was used at the beginning of year 8 for BGTSP421 (1mm Dow Corning MDX-4-4210 bond chip) and just before year 2 of the soak data for SP3GTA (3 mil Teflon® coated wire).

### Silicone Young's Modulus Testing

In order to further evaluate changes over time in the silicone materials of interest, the elasticity is being quantified. Elasticity was chosen because it reflects changes in cross linking of the polymer. According to Knoll *[W. Knoll, Chemistry and Technology of Silicones, San Diego: Academic Press, 1968, pp 494-500.]*, at least two competing reactions are thought to be at work during the aging of silicones in aqueous environments. One is the splitting off of organic groups which causes the formation of additional cross links. This process occurs under the influence of oxygen, particularly

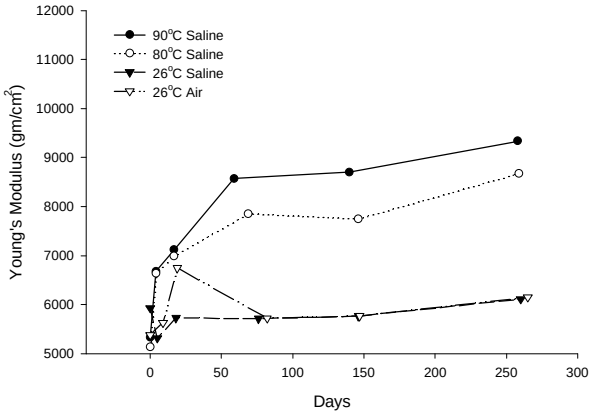
at elevated temperatures and stiffens and hardens the material. The other process is depolymerization which occurs in the presence of water. The net effect of these changes depends on ill defined parameters at the present time. However, at temperatures above 200°C, cross linking predominates leading to a brittle silica substance. In a closed system, void of oxygen, depolymerization predominates leading to a soft polymer.

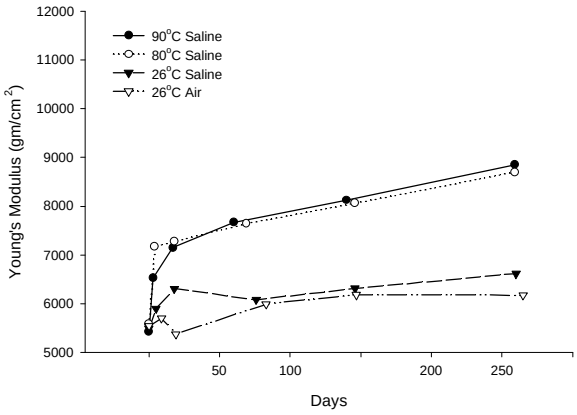
To begin to understand these issues for the materials we are evaluating, pull tests of samples of a representative silicone (CF20-2186 from Nusil) were begun eight months ago. Sixteen 20cm long rods of CF20-2186 silicone were cast using 2mm diameter Teflon tubing as a mold. Curing time was 3 hours for all cycles. All rods were cured at 50 C. Four of these rods received an additional air cure of 100°
received an air cure of 150°
200°
resulting o-ring structures were then pull tested on a simple pull system that used a sensitive computer interfaced ® balance for measurements. Measurements

steel rods that were moved by a micro-stepping linear actuator. The resulting slope of the force-displacement curves were then used to compute Young's modulus.

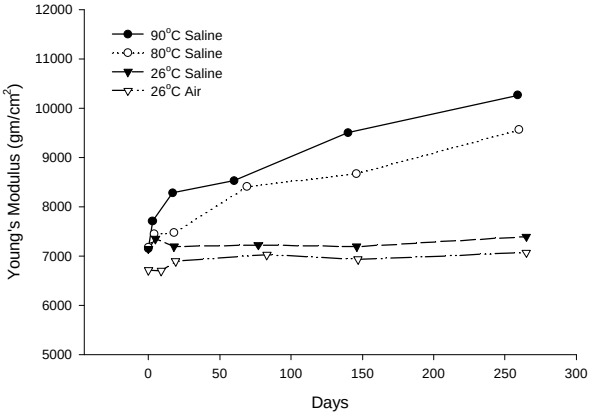
CF20-2186 Cured at 50°C Under Various Aging Environments

°C Under Various Aging Environments




CF20-2186 Cured at 150°C Under Various Aging Environments




CF20-2186 Cured at 200°C Under Various Aging Environments

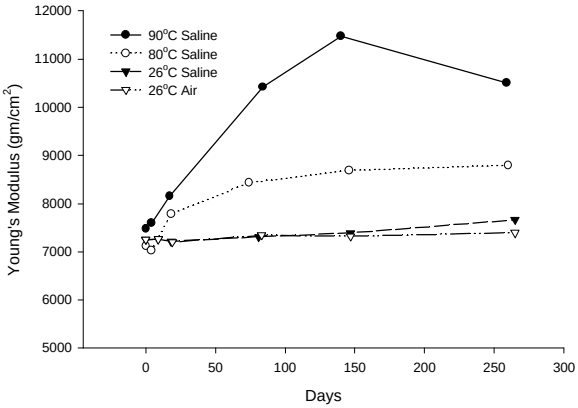


**Figure 3:** Young's modulus versus aging in days under various conditions for samples of Nusil CF20-2186 cured under various conditions.

One loop from each cure schedule group was placed in one of four environmental conditions: 1) 90°C saline, 2) 80°C saline, 3) 26°C saline, and 4) 26°C air. Periodically the loops were withdrawn from their aging environments and pull cycled. As shown in Figure 3, there is considerable variability in response to aging, but in general, there appears to be a stiffening of the material with time that is accelerated by elevated temperature saline soaks. The relationship between the cure schedule and the loss of elasticity is evident for the samples that are were not aged at elevated temperatures where the initial stiffness clearly related to the cure cycle as shown in Figure 4. Apparently there is a non-linear effect of cure temperature on the elasticity of the silicones which may in itself be significant for applications.

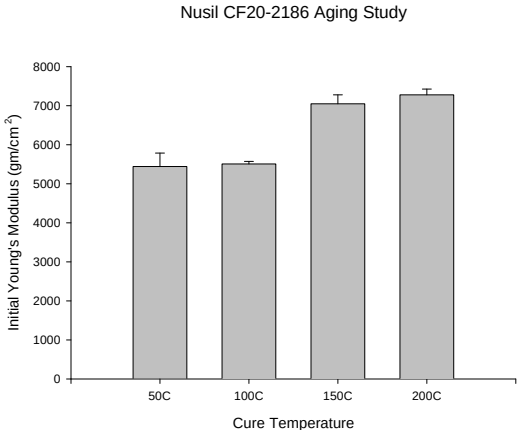



**Figure 4:** Initial elasticity modulus prior to aging for Nusil CF20-2186 samples cured at different temperatures. There were 4 samples in each group. Standard deviation is error bar.

## Silicone Adhesion Testing

Last quarter an initial test of silicone adhesion as measured by pull testing was reported. Subsequent refinement of the testing procedure resulted in more predictable force-displacement graphs. As shown in the data plot on the left in Figure 5, the peel force was a function of distance prior to complete delamination of the sample. By slowing the rate of stretching from 100µ/sec to 10µ/sec.

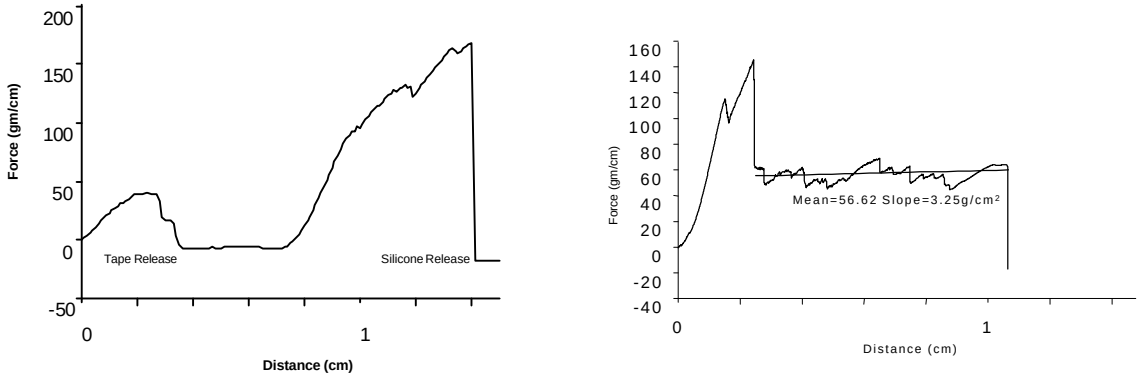


**Figure 5:** Silicone peel test examples on uncleaned silicon chips using fully cured Nusil CF20-2186. Note long, near zero slope exhibited by data on right taken from a pull test with a very slow pull rate compared to the data shown in the figure on the left.

The resulting data was remarkably consistent following an initial transient that was likely due to release of the tape used to attach to the silicone (it was double sided tape and the backside was attached to the substrate with the silicone attached to the frontside).

A variety of samples were prepared with different surface cleaning protocols, and cure schedules to identify critical points in silicone encapsulation methodology. This information will allow us to prepare more consistent samples, and will improve the odds that other laboratories will be able to duplicate our results using silicone encapsulants. 5 samples were prepared using portions of our standard silicon chip cleaning protocol followed by application of a 0.5cm wide stripe of Nusil MED-4220. The stripe of silicone overlapped a piece of Kapton tape with double sided silicone adhesive.

The simplest clean used "Pirhana" etch (2:1 conc $H_2SO_4$:30% $H_20_2$) followed by a de-ionized water rinse and $N_2$ blow dry. Results of this test are shown in Figure 6. The adhesion force exceeded the tensile strength of the material (431gm/cm) in contrast to the 56gm/cm adhesion strength measured for samples that were not cleaned prior to application of the silicone. Other samples that were tested had additional steps added to the basic clean: Pirhana plus isopropyl alcohol and $N_2$; Pirhana, isopropyl alcohol, $N_2$, and 150°C bake; Pirhana, isopropyl alcohol, $N_2$, 150°C bake and 30min UV-Ozone; and finally our complete standard clean of Pirhana, isopropyl alcohol, $N_2$, 150°C bake and 10min UV-Ozone. All of the samples exceeded the tensile strength of the silicone.

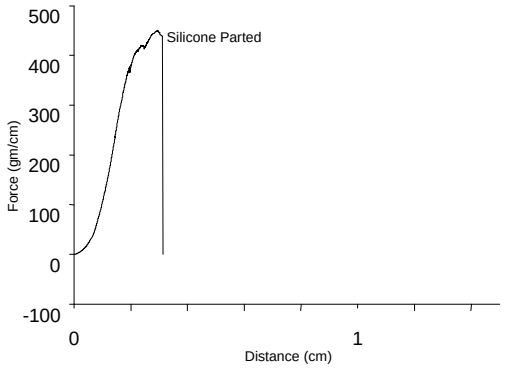



**Figure 6:** Pull test of sample prepared with only Pirhana clean and DI rinse. Adhesion exceeded the tensile strength of 0.5cm wide by ~1mm thick silicone piece.

Thus the good news of these experiments is that an aggressive surface cleaning is sufficient to substantially improve the bonding of silicone to the silicon dioxide surfaces. However, the methodology was insufficient to allow further differentiation of the effects of surface preparation. Perhaps using fiberglass cloth reinforcement of the silicone will allow testing of higher adhesion forces by improving the tensile strength of the pull tab. Fiberglass cloth strips may also be a convenient means of obtaining a well defined width of material being pulled.

## Fluoropolymer Research

The one long term PPECVD fluoropolymer material coated silicon test square continues to exhibit high bulk resistivity and freedom from observable corrosion (see Figure 7). Capacitance readings are also normal (230pF) indicating that the device is indeed connected to the measurement system and that the high resistance readings are real. From the capacitance reading, an exposed area of 0.4cm$^2$, and assuming a relative dielectric constant of 1.9 from prior work, the thickness of the film should be about 3μm. For this thickness, the bulk resistivity of the film would be about 4e16Ω-cm. While somewhat below the typical bulk resistivities for commercial Teflon® ($10^{17}$-$10^{18}$Ω-cm), the observed resistivity is very good compared to most materials and films we have tested.

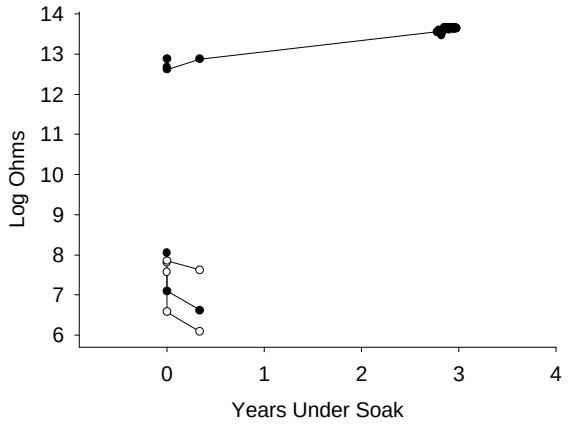



**Figure 7:** 90°C saline soak test results of fluoropolymer coated silicon surfaces. Test devices consisted of o-ring exposed flat surface coated with material under test.

## PPECVD Silicone Depositions

Development of silicone depositions from plasma sources continued. Additional experiments with 50/300 duty cycle and variations in argon flow further improved film flexibility. In order to allow implementation of the new silicone reactor, the old reactor was "de-commissioned" in December.

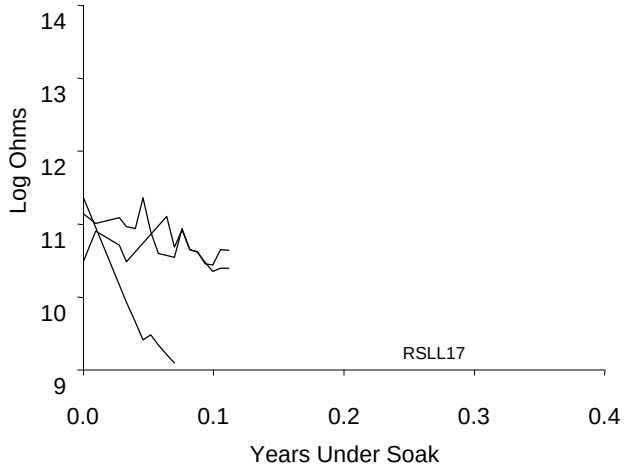


**Figure 8:** Short term soak data from 50 minute deposition using 50/300 duty cycle and 50cc/min argon.

Prior to this a set of new test devices using the 50/300 duty cycle and 50cc/min argon flow were fabricated. Four silicon squares coated with silicone (300pF, 0.4cm$^2$, $\varepsilon_r$~4 => 5μm thick) were assembled into long tubes for high temperature soak testing and placed under 80°C soak. Results are summarized in Figure 8. One device was excessively leaky upon submersion. A second device failed within a few weeks. 2 devices, however, are maintaining 7e$^{10}\Omega$ readings which is typical for the PPECVD silicone films under study.

A series of test devices were fabricated at a variety of test conditions. At the present time, a total of 68 test devices are under soak for evaluation of the PPECVD silicone films. While some have failed, most are holding in the 5e$^{10}\Omega$ range corresponding to a bulk resistivity of about 4e$^{13}\Omega$-cm which is in the right ball park for silicones. For example, control silicon squares coated with about 100 times the thickness of the PPECVD films exhibit bulk resistivity on the order of 8e$^{13}\Omega$-cm.

Wire samples, and assemblies of Michigan probes and triple track devices bonded out to 12 pin connectors were coated with PPECVD silicone but have not yet been assembled into test fixtures and tested. One of the issues with the assemblies is whether or not the wires near the bond sites are coated adequately. If not, it may be necessary to further encapsulate the wires prior to soak testing or implantation.

**Silicon Substrate Testing**

Since we began testing silicon nitride as a surface coating, we noticed that a very thin coating of silicone prevented dissolution of the silicon nitride. Since then a variety of surface tests were performed including implantation of double polished silicon pieces coated on one side by silicone. The original intent of this was to allow infiltration of biochemicals which could then be detected by differential FTIR spectroscopy.

However, removal of the silicon pieces 6 months later, revealed that the unprotected backside of the silicon had corroded to such an extent that the FTIR measurements could not be completed. This may indicate that silicon must be protected in some way to avoid corrosion. Since the University of Michigan program's devices had no protection for the underlying silicon substrate, this finding was significant. However, corrosion of UM devices had not been reported, so to determine if the P$^+$ substrates were somehow inherently corrosion proof, some example devices were obtained for testing. Devices were implanted subcutaneously and in the subdural space of a New Zealand rabbit and left in place for nearly one year. None of the devices showed any evidence whatsoever of corrosion of the substrate. In fact, the micro-pattern left by the boron etch stop process remained as well. There was some evidence of corrosion of the front surface of the structure evidenced by a rainbow effect on the dielectrics that was not previously noted. Further investigation of this and other aspects of the UM technology should be done.

A set of test devices was designed and submitted to UM for fabrication as shown in Figure 9, Figure 10, and Figure 11. These devices will allow evaluation of the

encapsulants and coatings for protection of contacts, surface leakage, and polysilicon. These devices can be used as subdural or intracortical implants. These should be available in Spring of 1999 for testing. Of particular interest will be the intracortical probes which can be used to evaluate insulating biomaterials within the neural tissue. The polysilicon interdigitated electrodes will allow monitoring of the surface dielectrics and the iridium electrodes will allow monitoring of deposited coatings.

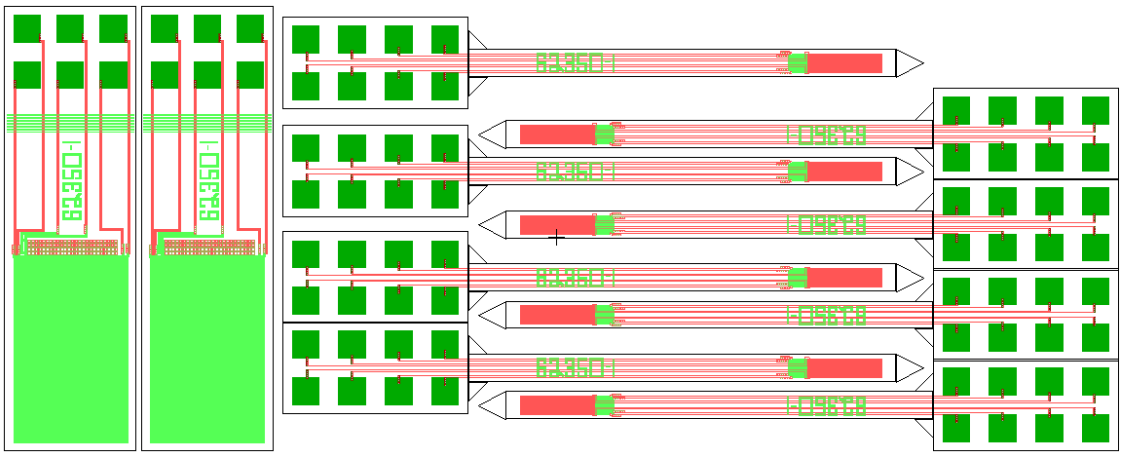


**Figure 9:** Interdigitated electrode arrays, contact strings, and brain probes for evaluation of dielectrics and encapsulants for the University of Michigan technology.

**Figure 10:** Enlarged section of UM Triple track device and contact string for evaluation of silicone encapsulants.

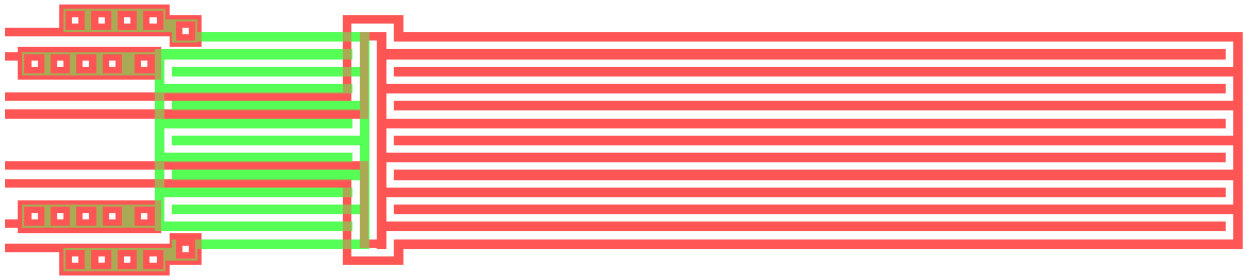


**Figure 11** Enlarged section of UM iridium and polysilicon interdigitated electrode arrays on cortical probes for evaluation of dielectrics and silicone PPECVD passivation.

**Integrated Circuit Test Chips**

The CMOS integrated circuits were received at the end of December and will be tested and evaluated next quarter. In view of the successful encapsulation of the lithium batteries, and LEDs for transmitting signals, if the integrated circuits do not function sufficiently well for implantation, then other CMOS test chips with functioning readouts but non-functioning sequencers will be assembled into a "power supply" monitor complete with LED telemetry and lithium batteries. These assemblies would output pulses at intervals that are functions of the implanted battery power. These implants will test the basic function of the CMOS integrated circuit in the body environment, and will also test the viability of the gold/aluminum or platinum/aluminum bonds. It will also test the interconnects between the batteries and chip, and the chip and the LED. However, if the new chips function satisfactorily, they will be implanted instead. Prior to implantation, all devices will be soak tested for at least two weeks until it is clear that they are functioning normally prior to implantation.

Improved modeling programs were obtained from Tanner Research and were used to evaluate the designs. It was noted that the transistor body effect was not properly taken into account during the previous design, and that there could be a clocking issue caused by improvements in the speed of the readout schmitt trigger. Accordingly, a new design was created in December and was felt to be enough of a step to warrant beginning fabrication prior to receipt of the current designs.

**Next Quarter:**

Additional modeling of the September, 1998 PassChip design will be used to determine if there is an appropriate operating point that will allow those devices to operate. The circuits will be tested and evaluated. If working circuits are available, implantable assemblies will be fabricated and soak tested in saline. If the circuits do not function, then implantable assemblies that simply transmit an encoded power supply level will be assembled and soak tested in saline to allow testing of the remainder of the circuit. An optimized detector for the transmitted signals will be fabricated. The band pass filter will be optimized for the wavelength and bandwidth of the transmitter LED output. An optimized detector will be designed for the low frequency transmitted pulse train. A 14 channel decoder and demultiplexer that will provide 14 analog outputs will be prototyped and tested on the working circuits from the September or December runs. If

all tests well, it may be possible to implant some new animals with the working system by the end of the quarter or beginning of the next quarter.